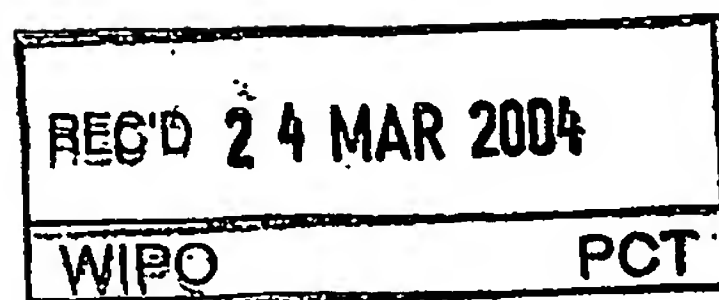


PCT/EP200 4 / 0 0 2 0 9 9

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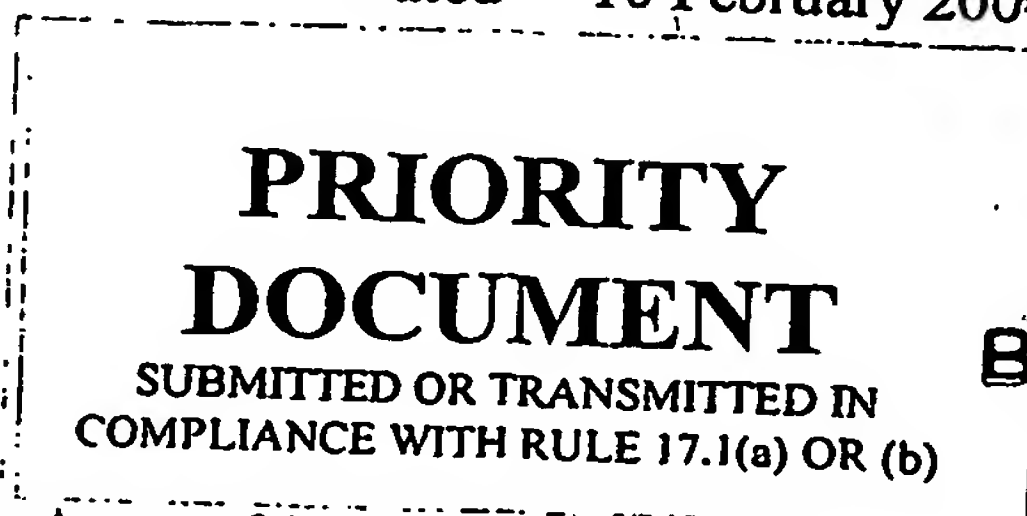
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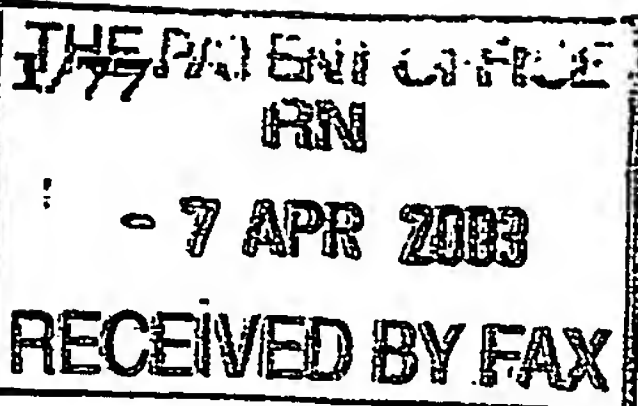
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MBZ-0520

2. Patent application number

(The Patent Office will fill in this part)

0307920.9

7 APR 2003

3. Full name, address and postcode of the or of each applicant (underline all surnames)

MBT Holding AG  
Vulkanstrasse 110  
CH-8048 Zürich  
Switzerland

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

7171101001  
Switzerland

4. Title of the invention

SHRINKAGE REDUCING ADDITIVE

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Mr. P. Brown  
FEB MBT  
Albany House  
Swinton Hall Road  
Swinton  
MANCHESTER M27 4DT

Patents ADP number (if you know it)

7178510001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
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  - c) any named applicant is a corporate body.
- See note (a))

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Continuation sheets of this form

Description

6

Claim(s)

4

Abstract

1

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents  
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11.

I/We request the grant of a patent on the basis of this application.

Signature

Date

07.04.2003

12. Name and daytime telephone number of person to contact in the United Kingdom

Mr. P. Brown, FEB MBT  
(0161) 794 7411

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# SHRINKAGE REDUCING ADDITIVE

This invention relates to the prevention of shrinkage in cementitious compositions and to materials for achieving this.

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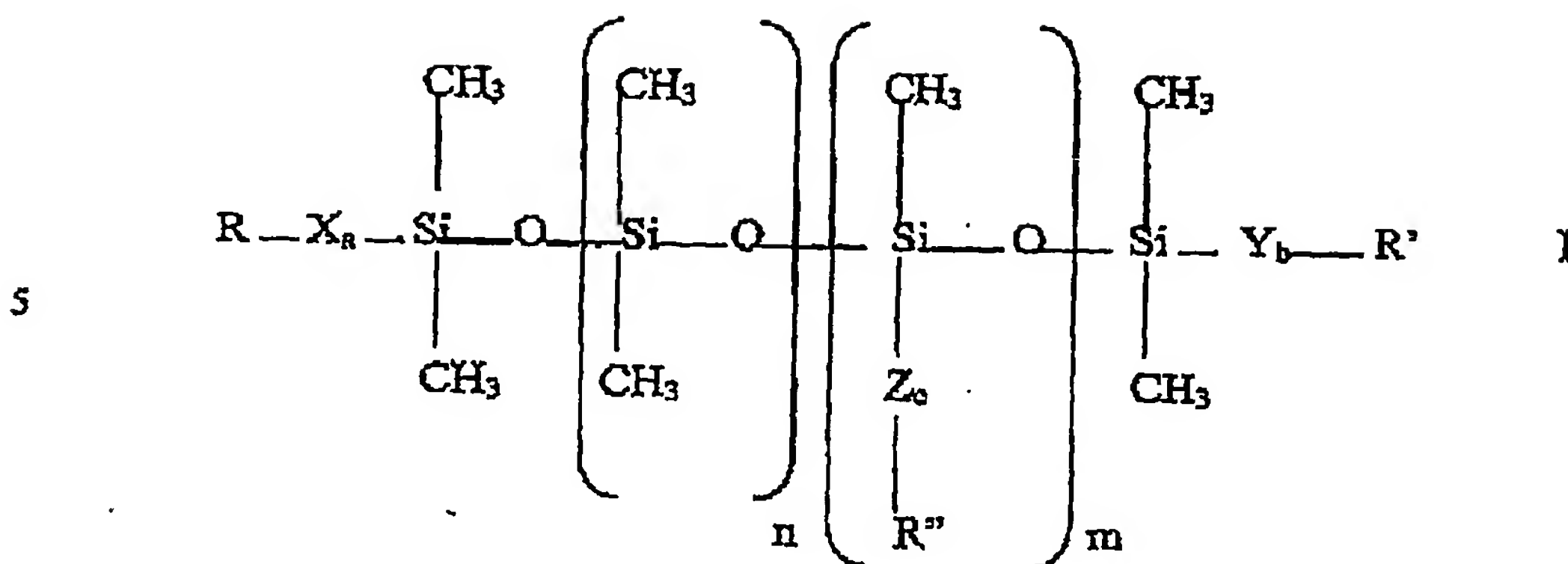
A commonly-encountered problem with cementitious compositions such as concrete and mortar is their tendency to shrink on drying after placement. This can cause some cracking, the presence of which can not only be unsightly but which also can allow the penetration of water into the cementitious composition. This can degrade the concrete  
10 by, for example, freezing and thawing in winter conditions, or by allowing water and/or aggressive chemicals to reach steel reinforcing embedded in the concrete, causing corrosion and reducing durability.

The subject has been intensively studied and a large patent literature is evidence of  
15 the commonness of the problem and the desirability of solving it.

It has now been found that a particular class of materials can reduce substantially the drying shrinkage of cementitious compositions. The invention therefore provides a method of reducing the drying shrinkage of a cementitious composition to which water  
20 has been added and the composition placed, comprising adding to the composition prior to placement at least one siloxane compound that is at least one of liquid and soluble in at least one of water and aqueous alkali.

By "siloxane compound" is meant any siloxane-based material, that is, a material having  
25 a linear or branched siloxane backbone chain of the form  $-\text{SiR}^a\text{R}^b-\text{O}-\text{SiR}^c\text{R}^d-\text{O}-$ . Any such material will work in this invention, provided that it is liquid or at least slightly soluble in at least one of water and aqueous alkali.

Preferred siloxane compounds for use in this invention are selected from those that  
30 correspond to the general formula I:



10 where m and n are independently from 1-2000, preferably from 1-500 and more preferably from 1-200, a, b, and c are independently either 0 or 1 and X, Y and Z are selected from

- 15
- O-;
  - O-(CH<sub>2</sub>)<sub>1-30</sub>-, this moiety being at least one of linear, branched and containing at least one ring;
  - (CH<sub>2</sub>)<sub>1-30</sub>-, this moiety being at least one of linear, branched and containing at least one ring;
  - CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-;
  - 20 -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CHOH-CH<sub>2</sub>-;
  - CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CHOH-CH<sub>2</sub>-O-;
  - CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CHOH-CH<sub>2</sub>-N-;

and R, R' and R'' are independently selected from at least one of hydrogen, C<sub>1-100</sub> alkyl, C<sub>6-30</sub> aryl, C<sub>7-30</sub> aralkyl; C<sub>7-30</sub> alkaryl; C<sub>1-30</sub> hydroxyalkyl; C<sub>3-200</sub> polyhydroxyalkyl; polyether consisting of from 2-200 identical or different C<sub>1-15</sub> oxyalkylene units, with the proviso that, if there is present more than one type of oxyalkylene unit, there shall be present at least two of each unit; C<sub>1-30</sub> aminoalkyl; polyiminopolyalkylene having from 1-20 identical or different C<sub>2-15</sub> alkylene units; polyiminopolyoxyalkylene having from 1-20 identical or different C<sub>2-15</sub> oxyalkylene units; C<sub>3-30</sub> quaternary ammonium, optionally completely or partially ionised with at least one anion; C<sub>4-30</sub> betaine; carboxyl, optionally completely or partially ionised with any suitable cation; C<sub>4-30</sub> polycarboxyalkyl, optionally completely or partially ionised with at least one cation; sulfo group,

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optionally completely or partially ionised with at least one cation; thiosulpho group, optionally completely or partially ionised with at least one cation; epoxide group; glycidyl; acrylate; C<sub>1-30</sub> ester; polyester consisting of from 2-200 C<sub>2-15</sub> diacid and diester monomer units; and esters of inorganic acids, all alkyl chains being at least one of linear, 5 branched and comprising at least one ring.

A more preferred class of siloxane compounds comprises those of Formula I in which a, b, and c are all 1 and X, Y and Z are selected from

- 10      -O-(CH<sub>2</sub>)<sub>1-30</sub>-, this moiety being linear or branched;  
          -(CH<sub>2</sub>)<sub>1-30</sub>-, this moiety being linear or branched;  
          -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CHOH-CH<sub>2</sub>-;

and R, R' and R'' are independently selected from at least one of hydrogen; hydroxy; 15 polyether consisting of from 2-200 identical or different C<sub>2-6</sub> oxyalkylene units, with the proviso that, if there is present more than one type of oxyalkylene unit, there shall be present at least two of each unit; C<sub>3-30</sub> quaternary ammonium, optionally completely or partially ionised with at least one anion; C<sub>4-30</sub> betaine; carboxyl, optionally completely or 20 partially ionised with at least one cation; sulpho group, optionally completely or partially ionised with at least one cation; thiosulpho group, optionally completely or partially ionised with at least one cation; glycidyl; and acrylate; all alkyl chains being at least one of linear, branched and comprising at least one ring.

An even more preferred class of siloxane compounds comprises those of Formula I in 25 which m and n are independently selected from 1-200, a, b, and c are all 1 and X, Y and Z are selected from

- 30      -O-(CH<sub>2</sub>)<sub>1-12</sub>;  
          -(CH<sub>2</sub>)<sub>1-12</sub>;  
          -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CHOH-CH<sub>2</sub>-;

and R, R' and R'' are independently selected from at least one of hydrogen; hydroxy; polyether consisting of from 2-200 identical or different C<sub>2-6</sub> oxyalkylene units, with the

proviso that, if there is present more than one type of oxyalkylene unit, there shall be present at least two of each unit; C<sub>3-30</sub> quaternary ammonium, optionally completely or partially ionised with at least one anion; C<sub>4-30</sub> betaine; carboxyl, optionally completely or partially ionised with at least one cation; glycidyl; and acrylate; all alkyl chains being  
5 capable of being linear or branched.

An even more preferred class of siloxane compounds comprises those of Formula I in which m is from 1-30 and n is from 1-100, a, b, and c are all 1 and X, Y and Z are selected from

10



15 and R, R' and R'' are independently selected from at least one of hydrogen; hydroxy; polyether consisting of from 2-200 identical or different C<sub>2-6</sub> oxyalkylene units, with the proviso that, if there is present more than one type of oxyalkylene unit, there shall be present at least two of each unit; C<sub>3-20</sub> quaternary ammonium, optionally completely or partially ionised with at least one anion; C<sub>4-10</sub> betaine and carboxyl, optionally completely  
20 or partially ionised with at least one cation; all alkyl chains being capable of being linear or branched.

The siloxanes hereinabove described may be any such material known to the art. Such materials are well known to the art for a variety of purposes, one of these being as  
25 antifoams in various industries. The preferred materials are those where R and R' are methyl or ethyl, n is from 5-200, more preferably from 10-150 and most preferably from 40-100, and m is from 1-100, more preferably from 2-40 and most preferably from 5-10.

The two different types of siloxane units may be arranged randomly or in blocks on the  
30 molecule. It is possible to utilise more than one type of moiety R''. Examples of R'' include ethylene oxide - propylene oxide copolymers of from 10 to 100 units.

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A polyether siloxane ("Tego" (trade mark) 2008 MR ex Degussa AG is used) is added to a concrete mix of the following composition:



|   |                 |     |                     |
|---|-----------------|-----|---------------------|
| 5 | Portland cement |     | 450 parts by weight |
|   | Aggregate       |     |                     |
|   | 0-4mm           | 770 | "                   |
|   | 4-8mm           | 440 | "                   |
|   | 8-16mm          | 440 | "                   |

W/C ratio 0.47

This mix is subjected to the shrinkage test of German Industrial Standard DIN 52 450, along with a mix that does not contain the siloxane.

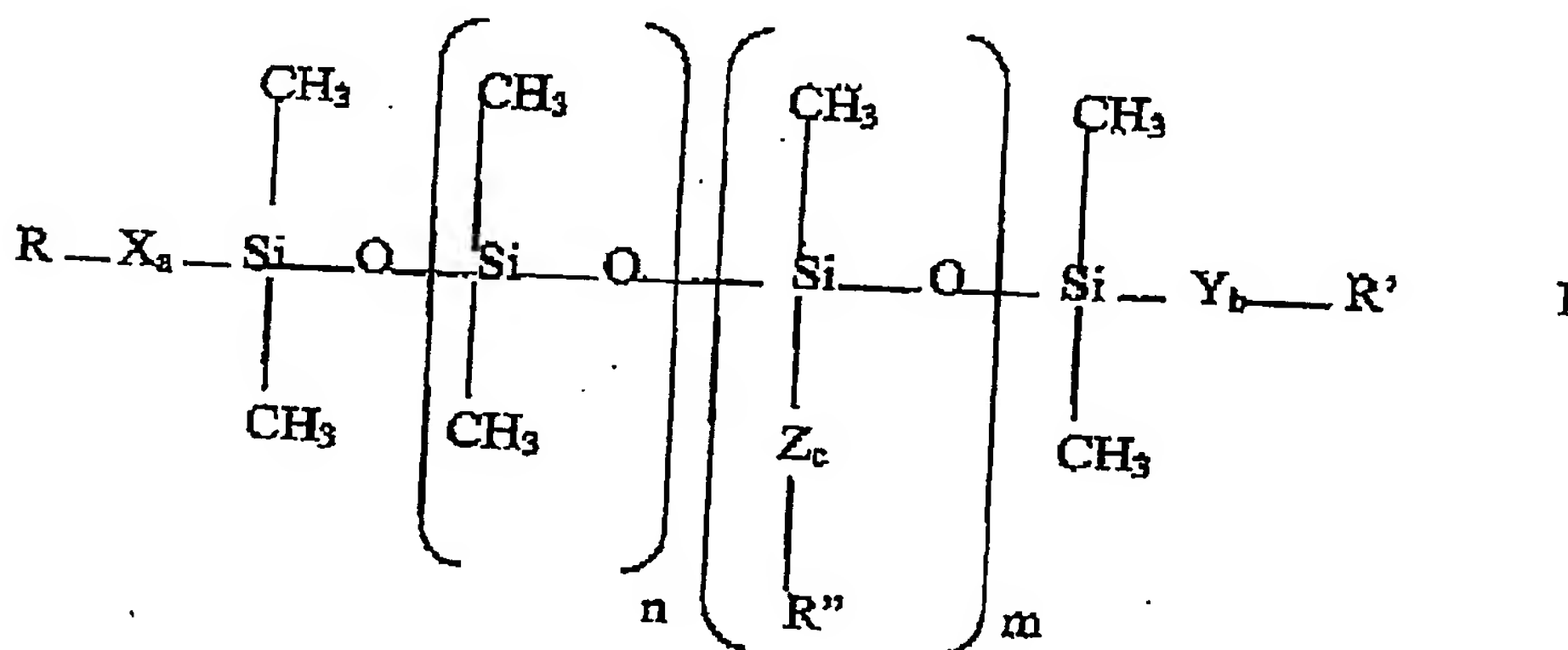
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The results are as follows:

| Age(days) |    | shrinkage (mm/M) |                  |
|-----------|----|------------------|------------------|
|           |    | with siloxane    | without siloxane |
| 15        | 1  | 0                | 0                |
|           | 3  | -0.119           | 0.029            |
|           | 7  | -0.074           | 0.157            |
|           | 10 | -0.006           | 0.195            |
|           | 14 | 0.057            | 0.225            |
| 20        | 28 | 0.082            | 0.349            |
|           | 42 | 0.17             | 0.405            |
|           | 49 | 0.193            | 0.418            |
|           | 59 | 0.167            | 0.396            |
|           | 70 | 0.244            | 0.48             |
| 25        | 80 | 0.271            | 0.503            |

## Claims:

1. A method of reducing the drying shrinkage of a cementitious composition to which water has been added and the composition placed, comprising adding to the composition prior to placement at least one siloxane compound that is at least one of liquid and soluble in at least one of water and aqueous alkali.
2. A method according to claim 1, in which the siloxane compound selected from those that correspond to the general formula I:



where m and n are independently from 1-2000, preferably from 1-500 and more preferably from 1-200, a, b, and c are independently either 0 or 1 and X, Y and Z are selected from

-O-;

-O-(CH<sub>2</sub>)<sub>1-30</sub>-, this moiety being at least one of linear, branched and containing at least one ring;

-(CH<sub>2</sub>)<sub>1-30</sub>-, this moiety being at least one of linear, branched and containing at least one ring;

-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-;

-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CHOH-CH<sub>2</sub>-;

-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CHOH-CH<sub>2</sub>-O-;

-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CHOH-CH<sub>2</sub>-N-;

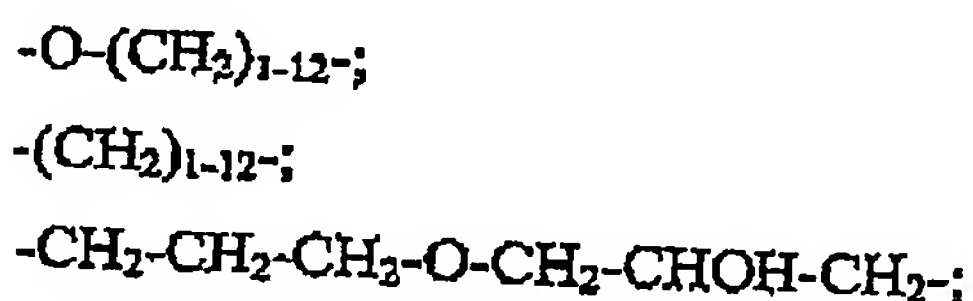
and R, R' and R'' are independently selected from at least one of hydrogen, C<sub>1-100</sub> alkyl, C<sub>6-30</sub> aryl, C<sub>7-30</sub> aralkyl; C<sub>7-30</sub> alkaryl; C<sub>1-30</sub> hydroxyalkyl; C<sub>3-200</sub> polyhydroxyalkyl; polyether consisting of from 2-200 identical or different C<sub>1-15</sub> oxyalkylene units, with the proviso that, if there is present more than one type of oxyalkylene unit, there shall be present at least two of each unit; C<sub>1-30</sub> aminoalkyl; polyiminopolyalkylene having from 1-20 identical or different C<sub>2-15</sub> alkylene units; polyiminopolyoxyalkylene having from 1-20 identical or different C<sub>2-15</sub> oxyalkylene units; C<sub>3-30</sub> quaternary ammonium, optionally completely or partially ionised with at least one anion; C<sub>4-30</sub> betaine; carboxyl, optionally completely or partially ionised with any suitable cation; C<sub>4-30</sub> polycarboxyalkyl, optionally completely or partially ionised with at least one cation; sulpho group, optionally completely or partially ionised with at least one cation; thiosulpho group, optionally completely or partially ionised with at least one cation; epoxide group; glycidyl; acrylate; C<sub>1-30</sub> ester; polyester consisting of from 2-200 C<sub>2-15</sub> diacid and diester monomer units; and esters of inorganic acids, all alkyl chains being at least one of linear, branched and comprising at least one ring.

3. A method according to claim 2, in which the siloxane compound of formula I is such that a, b, and c are all 1 and X, Y and Z are selected from

- O-(CH<sub>2</sub>)<sub>1-30</sub>-, this moiety being linear or branched;
- (CH<sub>2</sub>)<sub>1-30</sub>-, this moiety being linear or branched;
- CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CHOH-CH<sub>2</sub>-;

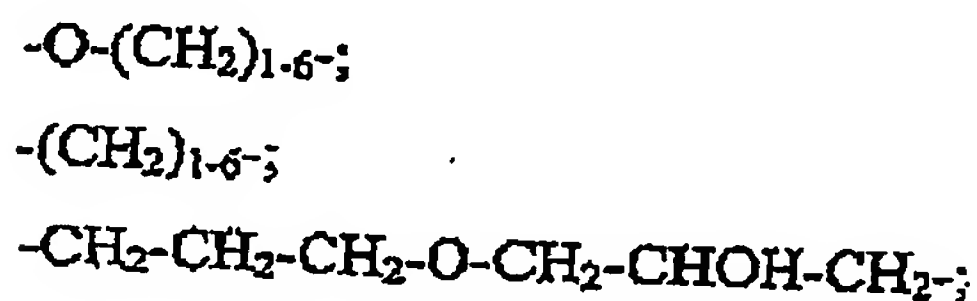
and R, R' and R'' are independently selected from at least one of hydrogen; hydroxy; polyether consisting of from 2-200 identical or different C<sub>2-6</sub> oxyalkylene units, with the proviso that, if there is present more than one type of oxyalkylene unit, there shall be present at least two of each unit; C<sub>3-30</sub> quaternary ammonium, optionally completely or partially ionised with at least one anion; C<sub>4-30</sub> betaine; carboxyl, optionally completely or partially ionised with at least one cation; sulpho group, optionally completely or partially ionised with at least one cation; thiosulpho group, optionally completely or partially ionised with at least one cation; glycidyl; and acrylate; all alkyl chains being at least one of linear, branched and comprising at least one ring.

4. A method according to claim 2, in which the siloxane compound of Formula I is such that m and n are independently selected from 1-200, a, b, and c are all 1 and X, Y and Z are selected from



and R, R' and R'' are independently selected from at least one of hydrogen; hydroxy; polyether consisting of from 2-200 identical or different C<sub>2-6</sub> oxyalkylene units, with the proviso that, if there is present more than one type of oxyalkylene unit, there shall be present at least two of each unit; C<sub>3-30</sub> quaternary ammonium, optionally completely or partially ionised with at least one anion; C<sub>4-30</sub> betaine; carboxyl, optionally completely or partially ionised with at least one cation; glycidyl; and acrylate; all alkyl chains being capable of being linear or branched.

5. A method according to claim 2, in which the siloxane compound of Formula I is such that m is from 1-30 and n is from 1-100, a, b, and c are all 1 and X, Y and Z are selected from



and R, R' and R'' are independently selected from at least one of hydrogen; hydroxy; polyether consisting of from 2-200 identical or different C<sub>2-6</sub> oxyalkylene units, with the proviso that, if there is present more than one type of oxyalkylene unit, there shall be present at least two of each unit; C<sub>3-20</sub> quaternary ammonium, optionally completely or partially ionised with at least one anion; C<sub>4-10</sub> betaine and carboxyl, optionally completely or partially ionised with at least one cation; all alkyl chains being capable of being linear or branched.

6. A method according to any one of claims 1-5, in which finely-divided silica is added to the cementitious composition.
7. A cementitious composition with reduced drying shrinkage, prepared by a method  
5 according to any one of claims 1-6.
8. A cementitious composition according to claim 7, in which the composition additionally contains finely-divided silica.



## ABSTRACT

- 5 A method of reducing the drying shrinkage of a cementitious composition to which water has been added and the composition placed, comprising adding to the composition prior to placement at least one siloxane compound that is at least one of liquid and soluble in at least one of water and aqueous alkali.

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